Colloidal lithography using silica particles: Improved particle distribution and tunable wetting properties

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ABSTRACT

Colloidal lithography rests on the adhesion of colloids in a relatively ordered pattern on a charged surface owing to electrostatic interactions. However, due to capillary forces, the colloids tend to form aggregates during the drying process. These capillary forces are especially strong for large hydrophilic particles. In this paper, different experimental approaches are explored to limit the aggregation of large (500 nm) silica particles deposited on glass substrates that were previously treated with polyallylamine (PAH), a polycation. These approaches consist in the addition of smaller colloids between the large ones, or of a layer of macromolecules (PAH or albumin) on top of the deposit. Scanning electron microscopy observations show that the addition of PAH and even better of albumin on top of the adherent colloids efficiently limits the formation of aggregates. Interestingly, the water contact angle of the surface obtained after silica colloid deposition and albumin adsorption is very high (∼95°), while very hydrophilic surfaces are obtained after calcination. This is discussed in light of the Wenzel and Cassie–Baxter models. In conclusion, the proposed method allows a nanoscale topographic pattern with tunable wettability to be created on large surface areas using a soft and inexpensive technique.

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1. Introduction

Colloidal lithography is based on the self-organization of nanoparticles on surfaces. This technique allows functionalizing large surface areas at the nanoscale level in a simple and effective way. A wide range of application fields including optics, catalysis, electronics, and biointerface design benefits from colloidal lithography [1–4]. In many cases, the pattern obtained by colloidal lithography serves as a basis for further elaboration of surface nanostructures. For example, colloidal lithography with polystyrene particles was used to produce surfaces presenting chemical nanoheterogeneities [5] as well as surfaces covered by gold nanorings showing particular optical properties [6]. The influence on protein adsorption and cell response of the nanotopography created by colloidal lithography has been widely studied [7–10].

When a colloidal solution enters in contact with a substrate, colloids deposit in a relatively ordered pattern as described by the random sequential adsorption model [11,12]. Colloid density on the surface depends on particle and substrate surface properties, in particular surface charges, particle size, and particle polydispersity and on the ionic strength and pH of the colloidal solution [13]. In several methods such as the Langmuir–Blodgett approach [14] or the colloidal convective assembly [15,16], the colloid layer deposited on a substrate is slowly dried in order to form closely-packed structures, known as colloid crystals, in which colloids are directly in contact with each other. Immersion capillary forces (F_{cap}), which act when the liquid film thickness (l_0) is close to the radius of the colloids, are responsible for this organization for particles with a radius inferior to ∼10 μm [17,18]. F_{cap} depends on surface tension γ of the liquid, particle radius R, and contact angle α between the liquid and the particle [17,19]. For the case of two spherical colloids, F_{cap} is defined by [17]:

$$F_{cap} \approx 2\pi\gamma r_c^2 (\sin^2 \Psi)(1/L) \qquad (1)$$

where, as illustrated in Fig. 1, r_c is the radius of the circle formed by the horizontal projection of the three-phases contact line at the particle surface, Ψ is the mean angle between the tangent of the meniscus at the contact line and a horizontal plane, and L is the distance between the centers of the particles. Hence, the attraction between particles increases when the contact angle α between the liquid and the particle surface decreases. The contact angle of the underlying substrate does however not have significant influence, and the effect of the disjoining pressure can be neglected as long as the liquid layer is not too thin, that is, the particle radius is large enough, which is the case for colloidal particles in the submicrometer range [19].

In many applications, keeping isolated and regularly distributed particles at the interface is desired [5–7,10]. In order to maintain
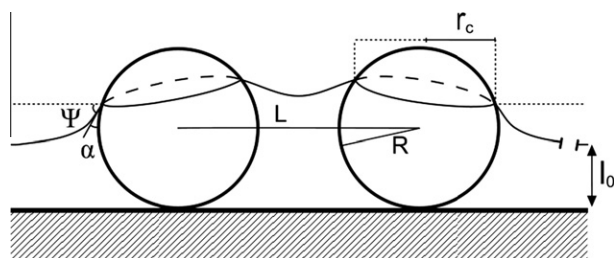
Fig. 1. Schematic representation of the liquid meniscus formed between two colloidal particles during the drying process. R is the radius of the colloids; L is the distance between the centers of the colloids; Ψ is the mean angle between the tangent of the meniscus at the contact line and a horizontal plane; α is the contact angle between the liquid and the particle; r_c is the radius of the circle formed by the horizontal projection of the three-phases contact line at the particle interface; and l_0 is the liquid film thickness (at a large distance from the particles). Figure adapted from Ref. [18].

the distribution of polystyrene colloids during the drying process, several methods have been developed to limit the effect of capillary forces [10,20]. A direct approach consists in reducing the capillary forces by using a liquid with a lower surface tension compared to water, such as isopropanol, before drying the surface [21]. An alternative approach is to increase the anchorage of the particles on the surface. For instance, charged colloids deposited on a surface covered by an oppositely charged polyelectrolyte are stabilized by electrostatic interactions [22]. The particle-surface interaction is increased as well by treating deposited polystyrene particles in boiling water, just above the glass transition temperature of the polymer, to increase the contact area, leading to an enhanced adhesion force [20]. The adsorption of small particles between larger colloids was also shown to reduce the formation of aggregates, which was attributed to steric repulsion [20]. Recently, a method was proposed to keep well-distributed silica particles at the solid-air interface after their transfer from a liquid-air interface. The approach rested on the surface modification of the particles to make them more hydrophobic and on the synthesis of a polymer brush ("grafting from" approach) at the solid surface [23]. Although this approach was shown to be successful, it is sophisticated, time-consuming, and lacks versatility.

Because capillary forces increase for larger particles having a low contact angle with the liquid phase used (see Eq. (1)), keeping a homogeneous distribution of large silica particles after drying remains challenging. This work explores different easy-to-implement and versatile strategies to stabilize the deposition pattern of large silica colloids from solution onto a glass substrate covered by polyallylamine hydrochloride (PAH), a polycation. The first explored strategy consists in the deposition of smaller colloids between the larger ones. In a second strategy, the colloidal deposit was covered by a layer of either PAH or albumin before drying. A combination of these two strategies was considered as well. Additionally, calcination was applied to remove all organic compounds involved in the process, allowing fully inorganic surfaces to be obtained. The morphology of the obtained samples was examined by scanning electron microscopy (SEM) coupled to image analysis, while their surface chemical composition was determined using X-ray photoelectron spectroscopy (XPS). Moreover, the water contact angle θ_w of the elaborated surfaces was measured.

2. Materials and methods

2.1. Materials

Glass substrates were squares of ~1.2 cm-side cut from microscope slides (Marienfield, Germany). PAH (Mw ~56,000 g/mol),

sodium hydroxide, colloidal silica dispersion (Ludox® TM-50, 50 wt.%, average diameter 30 nm [24]), and bovine serum albumin (essentially fatty acid free) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Silica colloids (9.83 wt.%, nominal diameter 500 nm, specific density 2.0 g/cm³) were purchased from Polysciences Inc. (Warrington, PA, USA). Water was ultrapure water (18.2 MΩ/cm) provided by an Elga Purelab Ultra device (Veolia, UK).

2.2. Sample preparation

The standard protocol for silica colloid deposition is inspired from the one used by Nonckreman et al. for polystyrene particle deposition [10]. Briefly, glass substrates were cleaned in piranha solution (H_2SO_4 cc/H_2O_2 (30%) 7:3), rinsed thoroughly with water, and immersed in vertical position for 30 min in 1.5 ml of a PAH 10^{-5} M solution at pH 11 (adjusted with sodium hydroxide). The samples were then rinsed six times with water. Each rinsing was performed without exposing the sample to air by adding 2 ml of rinsing liquid and removing 2 ml of solution. The samples were then gently dried under nitrogen and immersed in vertical position in a 0.1 wt.% suspension in water of 500 nm silica colloids for 2 h (pH 6.5, no salt added), rinsed three times with water and three times with isopropanol using the same rinsing procedure as the one described above, and dried in air overnight. Note that isopropanol is used with the aim to reduce capillary forces and hence to limit particle aggregation.

As shown in Fig. 2, three strategies were then implemented to the standard protocol in order to stabilize the colloidal layer before the final rinsing and drying steps. Therefore, modifications were brought to the standard protocol after the 500 nm colloid deposition. In contrast with the standard protocol, samples were rinsed six times with water after the 500 nm colloid deposition step. The first strategy then consisted in immersing the samples in a water suspension of 30 nm colloids at a concentration of 0.1 wt.%, rinsing three times with water and three times with isopropanol and drying in air overnight. The second strategy consisted in immersing the samples in a solution of either PAH (10^{-5} M at pH 11) or albumin (30 µg/ml in water, pH 6.5, no salt added) for 30 min in order to form a stabilizing adsorbed layer on top of the colloids. Then, samples were rinsed three times with water and three times with isopropanol and dried in air overnight. The third strategy combined the two previous ones and consisted in successively adding the smaller colloids, rinsing six times the samples with water, adding either the PAH or the albumin layer, rinsing three times with water and three times with isopropanol, and drying in air overnight. When indicated, the obtained dry samples were calcinated at 450 °C for at least 3 h in an oven (N3, Naber, Germany). Glass substrates only covered by a layer of PAH or albumin were prepared as reference samples for contact angle measurement.

2.3. Sample characterization

The samples were examined by SEM (Digital Scanning microscope 982 Gemini, Leo Electron Microscopy, UK) without adding any metal coating. SEM images were analyzed using ImageJ software. Briefly, image background was removed, a threshold value was defined to isolate particle edges, and particles were then filled in order to compute the surface coverage. For each condition, surface coverage was calculated on three images from different samples (~150 colloids counted on each picture). Centers of particles were extracted from representative images (i.e., the ones presented in Fig. 3) to calculate the radial distribution function with ImageJ radial profile plugin. This method considers all the particles in a given image and takes the edge effects into account.